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PATENT

Practitioner's Docket No.: 791_065 CON

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of: Hiroshi Nemoto and Kenshin Kitoh

Ser. No.: 09/997,604

Group Art Unit: 1745

Filed: November 29, 2001

Examiner: Susy N Tsang-Foster

Confirmation No.: 5235

For: LITHIUM SECONDARY BATTERY

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Janet M. Stevens

**TRANSMITTAL OF APPEAL BRIEF
(PATENT APPLICATION--37 C.F.R. § 1.192)**

1. Transmitted herewith, in triplicate, is the APPEAL BRIEF in this application, with respect to the Notice of Appeal filed on October 28, 2005.

2. STATUS OF APPLICANT

This application is on behalf of ☒ other than a small entity.
☐ a small entity.

3. FEE FOR FILING APPEAL BRIEF

Pursuant to 37 C.F.R. § 1.17(c), the fee for filing the Appeal Brief is:

☐ small entity \$250.00
☒ other than a small entity \$500.00

Appeal Brief Fee Due \$500.00

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4. EXTENSION OF TERM

The proceedings herein are for a patent application and the provisions of 37 C.F.R. § 1.136 apply.

(complete (a) or (b), as applicable)

- (a) ☒ Applicant petitions for an extension of time under 37 C.F.R. § 1.136 (fees: 37 C.F.R. §1.17(a)(1)-(5)) for the total number of months checked below:

Extension (months)		Fee for other than small entity	Fee for small entity
<input checked="" type="checkbox"/>	one month	\$ 120.00	\$ 60.00
<input type="checkbox"/>	two months	\$ 450.00	\$225.00
<input type="checkbox"/>	three months	\$ 1,020.00	\$510.00
<input type="checkbox"/>	four months	\$1,590.00	\$795.00
Fee			\$ 120.00

If an additional extension of time is required, please consider this a petition therefor.

(check and complete the next item, if applicable)

- [] An extension for _____ months has already been secured, and the fee paid therefor of \$ _____ is deducted from the total fee due for the total months of extension now requested.

Extension fee due with this request \$ _____

or

- (b) [] Applicant believes that no extension of term is required. However, this conditional petition is being made to provide for the possibility that applicant has inadvertently overlooked the need for a petition and fee for extension of time.

5. TOTAL FEE DUE

The total fee due is: Appeal brief fee \$ 500.00
 Extension fee (if any) \$ 120.00

TOTAL FEE DUE \$ 620.00

6. **FEE PAYMENT**

☒ Attached is a check in the sum of \$620.00.

☐ Charge Account No. _____ the sum of \$ _____.

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7. **FEE DEFICIENCY**

☒ If any additional extension and/or fee is required, this is a request therefor and to charge Account No. 50-1446.

AND/OR

☒ If any additional fee for claims is required, charge Account No. 50-1446.

Respectfully submitted,



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January 13, 2006

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Docket No.: 791_065 CON

PATENT
ON APPEAL

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE HONORABLE BOARD OF PATENT APPEALS AND INTERFERENCES

In re the application of: Hiroshi Nemoto and Kenshin Kitoh

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Janet M. Stevens

TRANSMITTAL OF BRIEF ON APPEAL

Sir:

Transmitted herewith are three copies of the Appellant's Brief on Appeal together with a check in the amount of \$620.00 to cover the fee under 37 CFR 1.17(c).

The Commissioner is hereby authorized to charge any additional fees associated with this communication or credit any overpayment to Deposit Account No. 50-1446.

Respectfully submitted,
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Enclosures: Brief on Appeal (3)



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BRIEF ON APPEAL

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REAL PARTY IN INTEREST

The real party in interest in the present appeal is NGK Insulators, Limited, the assignee in the present application.

II. RELATED APPEALS AND INTERFERENCES

There are no interferences or other appeals regarding this application or any application which is related to the present application.

III. STATUS OF CLAIMS

Claims 11-14, 16-21, 23 and 24 are pending.

Claims 11-14, 16-21, 23 and 24 stand finally rejected.

The applicants are appealing the rejections of claims 11-14, 16-21, 23 and 24 (these claims are set forth in Appendix A attached hereto).

IV. STATUS OF AMENDMENTS

No Amendment has been filed in this application after the presently-appealed final rejection (dated June 28, 2005).

V. SUMMARY OF CLAIMED SUBJECT MATTER

It is respectfully noted that the following concise explanation of the subject matter defined in each of the independent claims involved in the present appeal is provided only to comply with 37 C.F.R. 41.37, and that in order to ascertain the precise scope of each claim involved in the present appeal, it is necessary to refer to the text of each such claim, in its entirety, as set forth in Appendix A hereto.

Claim 13 recites a method of reducing internal resistance of a lithium secondary battery, comprising forming an electrode body, welding a plurality of current collecting portions directly to the positive electrode, and welding a plurality of current collecting portions directly to the negative electrode (specification, page 4, line 25 - page 5, line 11; page 18, lines 17-24).

Claim 13 recites that the electrode body is formed by placing a positive electrode and a negative electrode in contact with a separator, the separator being positioned between the positive electrode and the negative electrode, so that the positive electrode is not in contact with the negative electrode (specification, page 18, lines 17-21).

Claim 13 recites that the positive electrode comprises positive electrode active material which comprises Li and Mn (in a Li/Mn ratio of larger than 0.5) and which has a cubic spinel structure (specification, page 4, lines 8 and 18-19).

Claim 13 recites that primary particles of the positive electrode active material:

- have a substantially octahedral shape constituted mainly by flat crystal faces, and
- include particles having at least one side of each flat crystal face of length of 1 μm or more (specification, page 4, lines 9-15).

Claim 13 recites that the battery has a capacity of 2Ah or more (specification, page 4, line 24 - page 5, line 1).

Claim 17 recites a method of making a lithium secondary battery having low internal resistance and a capacity of 2 Ah or more, the method comprising welding a plurality of current collecting portions directly to a positive electrode which comprises a positive electrode active material (specification, page 4, line 25 - page 5, line 4; page 5, line 24 - page 6, line 1). The positive electrode active material is formed by forming a raw material mixture comprising Li and Mn and heating the raw material mixture to a temperature and for a time which is effective to convert the raw material mixture into a positive electrode active material which has a cubic spinel structure and in which primary particles of the positive electrode active material (1) have a substantially octahedral shape constituted mainly by flat crystal faces, and (2) include particles having at least one side of each flat crystal face of length of 1 μm or more (specification, page 5, lines 5-15; page 11, lines 5-10; page 12, lines 3-6).

VI. GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

1. Claims 12 and 19 are rejected under 35 U.S.C. §112, first paragraph.
2. Claims 11-14, 16-21, 23 and 24 are rejected under 35 U.S.C. §112, first paragraph.
3. Claims 11-14, 16-21, 23 and 24 are rejected under 35 U.S.C. §103(a), over Japanese 08-217452 (JP '452) in view of U.S. Patent No. 5,700,597 (Zhong '597) and U.S. Patent No. 6,106,975 (Watanabe '975).
4. Claims 11-14 and 16-21 and 23 are rejected under 35 U.S.C. §103(a) over U.S. Patent No. 5,631,104 (Zhong '104) in view of Zhong '597 and Watanabe '975.

5. Claims 11-14 and 16-21 and 23 are rejected under 35 U.S.C. §103(a) over U.S. Patent No. 5,961,949 (Manev '949) in view of Zhong '597 and Watanabe '975.

6. Claim 24 is rejected under 35 U.S.C. §103(a) over Zhong '104 in view of Zhong '597 and Watanabe '975, further in view of U.S. Patent No. 5,686,203 (Idota '203).

7. Claim 24 is rejected under 35 U.S.C. §103(a) over Manev '949 in view of Zhong '597 and Watanabe '975, further in view of U.S. Patent No. 5,686,203 (Idota '203).

VII. ARGUMENT

Issue 1 Rejection of claims 12 and 19 under 35 U.S.C. §112, first paragraph.

Claim 12 (dependent from claim 13) and claim 19 (dependent from claim 17) each recite that the primary particles *consist essentially of* (as opposed to “*including*”, as recited in each of claims 13 and 17) particles having at least one side of each flat crystal face of length of 1 μm or more.

The June 28, 2005 Office Action contains an assertion that the limitation “wherein said primary particles consist essentially of particles having at least one side of each flat crystal face of length of 1 μm or more” is not in the original disclosure.

The recitation in claims 12 and 19 that the primary particles *consist essentially of* particles having at least one side of each flat crystal face of length of 1 μm or more, means that within the scope of claims 12 and 19, the primary particles of the positive electrode active material can include non-conforming particles (i.e., particles which do not have at least one side of each flat crystal face of length of 1 μm or more), so long as there are not so many of such non-

conforming particles that the basic and novel characteristics of the present invention are materially affected. That is, as has been repeatedly and consistently held, the expression "consisting essentially of" renders the claim open only for the inclusion of unspecified ingredients which do not materially affect the basic and novel characteristics of the claimed invention. Those basic and novel characteristics of the invention include significant reduction in internal resistance and good repeated cycle properties, as described throughout the present specification (e.g., page 2, line 23 - page 3, line 4; page 4, line 25 - page 5, line 4; page 15, line 18 - page 17, line 17).

The original specification, page 5, lines 12-15, discloses that the primary particles preferably contain primary particles in which at least one side of each flat crystal face has a length of 0.2 μm , or more preferably, 1 μm or more. The original specification, page 8, lines 21-23, discloses that "[t]he positive electrode active material used in the present lithium secondary battery is characterized by consisting of primary particles mostly having the above-mentioned [i.e., substantially octahedral shape] morphology." The original specification, page 8, lines 23-24, discloses that all the primary particles need not have a substantially octahedral shape.

These portions of the specification demonstrate that the present inventors had possession of the claimed subject matter. The statement referred to in the June 28, 2005 Office Action (page 3, lines 13-14) that all the primary particles *need not* have a substantially octahedral shape (original specification, page 8, lines 23-24) (1) confirms that the specification contemplates subject matter in which *all* primary particles have a substantially octahedral shape, and (2) indicates that the invention nonetheless covers subject matter in which less than all of the primary particles have a substantially octahedral shape.

Claims 12 and 19, by virtue of their dependencies on claims 10 and 17, respectively, recite that the primary particles have a *substantially* octahedral shape. The original specification, page 8, lines 7-20, notes that the expression "substantially octahedral shape" includes not just primary particles having octahedral shape, but also primary particles of other shapes, namely, (a) particles wherein the apex formed by intersection of four crystal faces is not complete and is in the form of a plane or an edge, (b) particles in which a different crystal face is formed at an edge formed by intersection of two crystal faces, and (c) particles in which one crystal face is jointly owned by two primary particles or in which a primary particle grows from the surface of another primary particle, as well as shapes formed by partial chipping of the above shapes or joint possession of crystal faces between two primary particles.

The Office Action further contains a statement that

. . . it would be impossible to produce a positive electrode active material consisting essentially of primary particles in which at least one side of each flat crystal face of the particle has a length of 1 micron or more since not all primary particles are substantially octahedral in shape constituted mainly by flat crystal faces since some particles formed may be round and not have a flat crystal face.

(June 28, 2005 Office Action, page 3, lines 6-10). In response, it is respectfully noted that, as set forth above, the recitation in claims 12 and 19 that the primary particles *consist essentially of* particles having at least one side of each flat crystal face of length of 1 μm or more means that the primary particles of the positive electrode active material can include non-conforming particles, so long as there are not so many of such non-conforming particles that the basic and novel characteristics of the present invention are materially affected. In addition, the U.S. PTO provides no basis for any implication that it would be impossible to produce positive electrode

active material consisting essentially of particles having a substantially octahedral shape constituted mainly by flat crystal faces and including particles having at least one side of each flat crystal face of length of 1 μm or more, in which the amount of and/or shape of any non-conforming particles are such that the basic and novel characteristics of the present invention are not materially affected.

The present specification discloses that production of the positive electrode active material of the present invention is conducted by firing a raw material mixture consisting of given proportions of salts and/or oxides of various elements in an oxidizing atmosphere at 700 to 900°C for five to fifty hours (original specification, page 11, lines 5-10). The specification further discloses that when the firing temperature is low, growth of particles hardly takes place, making it difficult to obtain a positive electrode active material constituted by primary particles having intended particle diameters and an intended shape, whereas when the firing temperature is high, large primary particles are formed but neck growth occurs between primary particles and each neck portion becomes rounded (original specification, page 11, lines 11-17). Thus, the specification discloses, by selecting the composition of raw materials and the firing conditions appropriately, it is possible to control the average particle diameter of the primary particles obtained and the morphology of the primary particles (original specification, page 12, lines 3-6).

For example, the specification discloses, in the positive electrode active material of comparative example 2, in which a positive electrode active material was obtained by weighing and mixing powders of Li_2CO_3 , MnO_2 and B_2O_3 and then firing the resulting mixture in an oxidizing mixture at 800°C for twenty-four hours, striking particle growth was observed and the primary particles were roundish, and that primary particles having a substantially octahedral

shape could be obtained by lowering the synthesis temperature and/or shortening the synthesis time in order to suppress the particle growth (original specification, page 12, lines 6-12 and page 14, lines 10-14).

The Office Action further contains a statement that the specification "states that the particle diameters of the primary particles are obtained by analysis of the SEM image and the particle diameter measurement for individual particles are impossible." (June 28, 2005 Office Action, page 3, lines 17-19) This statement leaves out a critical portion of the statement in the specification to which it refers. In particular, the statement in the specification reads "[t]he particle diameters of the primary particles are expressed as particle diameters obtained by the analysis of SEM image because the separation of individual particles and the particle diameter measurement for individual particles are impossible." The complete statement in the specification clearly describes that particle diameters of the primary particles are expressed as particle diameters obtained by the analysis of SEM image, and that the reason particle diameters of the primary particles are expressed in this way is because the separation of individual particles is impossible. This statement in no way indicates that measurement of particle diameters of the primary particles is impossible.

The Office Action further contains a statement that

[t]he specification also states . . . that the amount of primary or secondary particles having particle diameters outside the specified ranges are at such a level not ordinarily detected in the methods of measurement for particle diameters mentioned in the specification.

(June 28, 2005 Office Action, page 3, lines 19-22). As noted above, the recitation "consisting essentially of" does not require that *every* primary particle satisfy the recited feature, but rather

that the amount (if any) of primary particles not satisfying the recited feature is not so large as to materially affect the basic and novel characteristics of the present invention. The above-quoted statement in the Office Action is not inconsistent with the statements in the present specification that the subject matter recited in claims 12 and 19 can be made and used as disclosed in the present specification.

Accordingly, for the reasons set forth above, the original specification contains a written description of the subject matter claimed in claims 12 and 19

Issue 2 **Rejection of claims 11-14, 16-21, 23 and 24 under 35 U.S.C. §112, first paragraph.**

The Office Action acknowledges that the specification is enabling for forming a positive electrode comprising $\text{Li}(\text{Ni}_{0.5}\text{Ti}_{0.5})_{0.15}\text{Mn}_{1.85}\text{O}_4$. The Office Action contains a statement that “[t]he claimed invention encompasses compounds that are outside the scope of the one working example and disclosure” (June 28, 2005 Office Action, page 4, lines 20-21) and that “. . . undue experimentation would be required to determine what other compounds other than those disclosed by Applicant can be used to make and practice applicant’s invention as claimed.” (June 28, 2005 Office Action, page 5, lines 7-9).

The Office Action further contains statements that the specification “. . . does not reasonably provide enablement for forming all positive electrode material comprising mainly Li and Mn . . .” (June 28, 2005 Office Action, page 4, lines 7-13). The Office Action further contains a statement that “[t]he specification does not enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make the invention commensurate

in scope with these claims.” (June 28, 2005 Office Action, page 4, lines 17-19).

The U.S. PTO, however, has not provided any explanation as to why it doubts the truth or accuracy of the statements in the present application that the present invention is operable as disclosed, e.g., in the original specification, page 12, lines 3-12.

The U.S. PTO, in rejecting a claim under enablement requirement of 35 U.S.C. 112, bears the initial burden of setting forth a reasonable explanation of why the scope of protection provided by a claim is not adequately enabled by the specification's description of invention, and this burden includes providing sufficient reasons for doubting any assertions in specification as to the scope of enablement. If the U.S. PTO meets this burden, then the burden shifts to applicant to provide suitable proofs indicating that specification is enabling. *In re Wright* 27 USPQ2d 1510, 1514 (Fed. Cir. 1993). With regard to proof of utility and operability of inventions, an invention is presumed to be operable as disclosed. The burden shifts only if there is a reasonable doubt as to the truth of the applicants' assertions. Accordingly, a rejection for lack of enablement can only be made if there is reason to doubt the objective truth of the statements that the invention would be useful as disclosed in the specification. Thus, whenever a rejection on this basis is made, it is incumbent upon the U.S. PTO to explain *why* it doubts the truth or accuracy of a statement in a supporting disclosure, and to back up assertions of its own with acceptable evidence or reasoning which is inconsistent with the contested statement. *In re Marzocchi & Horton*, 169 USPQ 367, 369 (CCPA 1971).

A specification which contains a teaching of the manner and process of making and using the invention in terms which correspond in scope to those used in the claims must be accepted as satisfying the enablement requirement unless there is reason to doubt the objective truth of the

statements in the specification. Accordingly, it is incumbent upon the USPTO, whenever a rejection is made on the basis of such doubt, to explain why it doubts the truth or accuracy of any statement in the disclosure and to back up assertions of its own with acceptable evidence or reasoning which is inconsistent with the contested statement. *In re Armbruster*, 185 USPQ 152, 153 (CCPA 1975). As noted above, the U.S. PTO has not provided any such explanation.

The June 28, 2005 Office Action merely refers to a comparative example (Comparative Example 1) in the present specification, in which raw materials obtained by mixing Li_2CO_3 , MnO_2 and B_2O_3 were fired at 800 °C for 24 hours, and the resulting product did not meet the features recited in the present claims. Such material is accordingly outside the scope of the present invention. A skilled artisan would therefore not repeat a procedure using the same raw materials, temperature and duration of heating in an attempt to provide positive electrode active material according to the present invention. Instead, a skilled artisan would change one of the raw materials or the relative proportions of the raw materials, the temperature and/or the duration of heating. In view of the disclosure in the present specification, page 11, lines 5-17 and page 12, lines 6-12 and page 14, lines 10-14, a skilled artisan might try heating the same raw materials to a lower temperature or heat for a shorter period of time.

In addition, the enablement requirement of 35 U.S.C. 112 does not require that an applicant describe each combination of raw materials and heating regimens which would result in positive active material which is outside the scope of the claims. The specification contains guidance which would enable persons of skill in the art to arrive at combination which produce positive active material which is within the scope of the claims. For comparison, see *In re Fuetterer*, 138 USPQ 217, 223 (CCPA 1963), in which the USPTO objected to the breadth of

certain claims, stating that there would be an undue burden placed upon the public to determine what salts are suitable for obtaining the desired results, and then the CCPA held that there is no requirement that an applicant discover which of all the salts within the generic expression in the claim would function properly in the invention.

Accordingly, for the reasons described above, the original specification provides an enabling description of the subject matter recited in claims 11-14, 16-21, 23 and 24.

Issue 3 **Rejection of claims 11-14, 16-21, 23 and 24 under 35 U.S.C. §103(a), over Japanese 08-217452 (JP ‘452) in view of U.S. Patent No. 5,700,597 (Zhong ‘597) and U.S. Patent No. 6,106,975 (Watanabe ‘975).**

Claim 13 is directed to a method of reducing internal resistance of a lithium secondary battery. The method comprises forming an electrode body which includes a positive electrode comprising positive electrode active material, the primary particles of which have a substantially octahedral shape constituted mainly by flat crystal faces, such primary particles including particles having at least one side of each flat crystal face of length of 1 μm or more. The method recited in claim 13 further comprises welding a plurality of current collecting portions directly to the positive electrode, and welding a plurality of current collecting portions directly to the negative electrode.

Claim 17 recites a method of making a lithium secondary battery having low internal resistance, the method comprising welding a plurality of current collecting portions directly to a positive electrode which comprises a positive electrode active material. Claim 17 also recites that the positive electrode active material is formed by forming a raw material mixture comprising Li and Mn and heating the raw material mixture to a temperature and for a time

which is effective to convert the raw material mixture into a positive electrode active material which has a cubic spinel structure and in which primary particles of the positive electrode active material (1) have a substantially octahedral shape constituted mainly by flat crystal faces, and (2) include particles having at least one side of each flat crystal face of length of 1 μm or more.

JP '452 is directed to a *needle-like* particle shape manganese complex oxide (JP '452, English-language translation provided by the U.S. PTO – Appendix D, page 8, paragraph [0107], line 8; title). The U.S. PTO is attempting to ignore the express statements in JP '452 that the particles of JP '452 are *needle-like*. In particular, the U.S. PTO characterizes the disclosure in JP '452 of *needle-like* regular octahedral shaped particles as octahedral, i.e., the U.S. PTO has attempted to eliminate from the disclosure in JP '452 the expression "needle-like." To the contrary, a regular octahedron needle-like particle consists of a pair of regular octahedral-shaped end regions having an extension portion therebetween, rendering the particle "needle-like." That the expression in JP '452 of "needle-like regular octahedron" indicates that the structure is not regular octahedron in shape, is analogous to the fact that a "truncated cone" is not of a cone shape.

Similarly, the needle-like regular octahedron shapes disclosed in JP '452 do not fall within any of the definitions of "substantially octahedral shape" contained in the present specification, i.e., (a) particles wherein the apex formed by intersection of four crystal faces is not complete and is in the form of a plane or an edge, (b) particles in which a different crystal face is formed at an edge formed by intersection of two crystal faces, and (c) particles in which one crystal face is jointly owned by two primary particles or in which a primary particle grows from the surface of another primary particle, as well as shapes formed by partial chipping of the above

shapes or joint possession of crystal faces between two primary particles.

In addition, attached hereto (Appendix E) is a good quality image of Figs. 3 and 4 of JP '452 which shows that the particles therein are not regular octahedral (see in particular the particle marked with an asterisk on a second attached copy (Appendix F) of Figs. 3 and 4 of JP '452).

The Office Action further contains a statement that ". . . since the positive electrode active material has the same particle shape, composition, and primary particle size as those disclose in the specification and being claimed in the instant claims, the primary particles inherently include particles having at least one side of each flat crystal face of length of 1 micron or more."

It is respectfully noted that in order for principles of inherency to apply, the missing descriptive material must *necessarily* be present, not merely probably or possibly present, in the prior art. *In re Robertson*, 169 F.3d 743, 745, 49 USPQ2d 1949, 1950-51 (Fed. Cir. 1999), citing *Continental Can Co. USQ, Inc. v. Monsanto Co.*, 948 F.2d 1264, 1268, 20 USPQ2d 1746, 1749 (Fed. Cir. 1991).

The present specification discloses that production of the positive electrode active material of the present invention is conducted by firing a raw material mixture consisting of given proportions of salts and/or oxides of various elements in an oxidizing atmosphere at 700 to 900°C for five to fifty hours (original specification, page 11, lines 5-10). The specification indicates that for each particular combination of raw materials, the heating regimen must be selected from within this generic disclosure, and that firing a combination of raw materials which conforms to the description of raw materials employed according to the present invention in a heating regimen within the generic disclosure for the present invention, one does not necessarily

obtain a product having the claimed morphology. For example, the specification discloses that when the firing temperature is low, growth of particles hardly takes place, making it difficult to obtain a positive electrode active material constituted by primary particles having intended particle diameters and an intended shape, whereas when the firing temperature is high, large primary particles are formed but neck growth occurs between primary particles and each neck portion becomes rounded (original specification, page 11, lines 11-17). Thus, the specification discloses, by selecting the composition of raw materials and the firing conditions appropriately, it is possible to control the average particle diameter of the primary particles obtained and the morphology of the primary particles (original specification, page 12, lines 3-6).

For example, the specification discloses, in the positive electrode active material of comparative example 2, in which a positive electrode active material was obtained by weighing and mixing powders of Li_2CO_3 , MnO_2 and B_2O_3 and then firing the resulting mixture in an oxidizing mixture at 800°C for twenty-four hours, striking particle growth was observed and the primary particles were roundish, and that primary particles having a substantially octahedral shape could be obtained by lowering the synthesis temperature and/or shortening the synthesis time in order to suppress the particle growth (original specification, page 12, lines 6-12 and page 14, lines 10-14).

Even within the broad description of the process set forth in the present specification, page 11, lines 5-10, obtaining the properties recited in the present claims is clearly not inherent. With the guidance provided in the present specification (e.g., page 12, lines 9-12), persons of skill in the art are provided with the information needed in order to be readily able to produce positive active material which does satisfy the parameters recited in the claims by appropriate

selection of raw materials and firing conditions within the scope of the process described in page 11, lines 5-10, without having to engage in an undue amount of experimentation.

Without the guidance provided by the present specification or the subject matter recited in the present claims, persons of skill in the art would have no reason to attempt to make selections from within the broad disclosure in JP '452 so as to arrive at a battery having a positive electrode comprising positive electrode active material which satisfies the features recited in the present claims. In fact, JP '452 instead motivates persons of skill in the art to attempt to select process conditions and raw materials so as to obtain *regular octahedron needle-like* particles which are then used as a positive electrode active substance.

As noted above, the present invention is directed to a method of *reducing internal resistance* of a lithium secondary battery, and JP '452 does not address (or otherwise disclose or suggest) reducing internal resistance. The particle shape recited in the present claims contributes to the reduction of internal resistance according to the present invention.

In addition, JP '452 does not disclose or suggest welding a plurality of current collecting portions directly to the positive electrode or welding a plurality of current collecting portions directly to the negative electrode. In addition, JP '452 does not address (or otherwise disclose or suggest) reducing internal resistance. The welding of a plurality of current collecting portions directly to the positive electrode (recited in claims 13 and 17) and the welding of a plurality of current collecting portions directly to the negative electrode (recited in claim 13) contribute to the reduction of internal resistance according to the present invention.

The June 28, 2005 Office Action contains a statement that

[t]he JPO machine translation of JP 08-217452 A does not disclose welding a plurality of current collecting portions directly to the positive electrode and to the negative electrode and that the battery has a capacity of 2 Ah, and that the battery is used in an electric vehicle or a hybrid electric vehicle.

(June 28, 2005 Office Action, page 11, lines 17-20).

The U.S. PTO relies on Zhong '597 for alleged disclosure of a lithium battery as a high energy density source for an electric vehicle (June 28, 2005 Office Action, page 11, lines 21-22), and the U.S. PTO relies on Watanabe '975 for alleged disclosure of ultrasonically welding a plurality of tabs directly to the positive electrode and to the negative electrode (June 28, 2005 Office Action, page 12, lines 13-16).

Neither the alleged disclosure in Zhong '597 relied on in the June 28, 2005 Office Action nor the alleged disclosure in Watanabe '975 relied on in the June 28, 2005 Office Action contains any suggestion or motivation to modify the methods or materials employed in JP '452 so as to arrive at a method in which primary particles of the positive electrode active material have a substantially octahedral shape constituted mainly by flat crystal faces, the primary particles including particles having at least one side of each flat crystal face of length of 1 μm or more. In addition, the batteries disclosed in Watanabe '975 differ in many ways from the batteries disclosed in JP '452, and Watanabe '975 does not contain disclosure which would indicate that welding current collecting portions directly to the positive electrode of JP '452 would achieve any advantage.

Accordingly, no combination of JP '452, Zhong '597 and Watanabe '975 would render obvious any of the subject matter recited in claims 11-14 and 16-21, 23 and 24.

Issue 4 Rejection of claims 11-14 and 16-21 and 23 under 35 U.S.C. §103(a) over U.S. Patent No. 5,631,104 (Zhong '104) in view of Zhong '597 and Watanabe '975.

Zhong '104 discloses high voltage insertion compounds for lithium batteries (Zhong '104, title). Zhong '104 discloses insertion compounds having the formula $\text{Li}_{x+y}\text{M}_z\text{Mn}_{2-y-z}\text{O}_4$, wherein the crystal structure is spinel-like, M is a transition metal, $0 \leq x < 1.0$, $0 \leq y < 0.33$, and $0 < z < \text{about } 1$ (Zhong '104, abstract). Zhong '104 does not disclose that the particles disclosed therein have any particular shapes.

The June 28, 2005 Office Action includes a statement that

[s]ince Zhong et al. disclose identical synthesis conditions and formulas for the positive electrode active material in the lithium battery . . . as those of the applicants, the properties cited in the instant claims . . . are inherent in the positive electrode active material of Zhong et al.

(June 28, 2005 Office Action, page 15, lines 3-7).

As discussed above, and as demonstrated in the Example and Comparative Examples in the present specification, processing positive electrode active material and satisfying merely the features described in the present specification, page 11, lines 5-10 (namely, firing a raw material mixture consisting of oxides of various elements, including Li, Mn and as necessary, a substitution element(s) and an addition element(s), in an oxidizing atmosphere at 700 to 900 °C), does not *inherently* result in production of positive electrode active material having the characteristics recited in the present claims. With the guidance provided in the present specification (e.g., page 12, lines 9-12), persons of skill in the art are provided with the information needed in order to be readily able to produce positive active material which does

satisfy the parameters recited in the claims by appropriate selection of raw materials and firing conditions within the scope of the process described in page 11, lines 5-10.

The specification includes description of an Example in accordance with the present invention, in which a positive electrode active material was produced which consisted of primary particles having a substantially octahedral shape.

The procedures described in Zhong '104 clearly differ from the method used in the Example. There is no basis for the statements in the Office Action to the effect that Zhong '104 discloses identical synthesis conditions and formulas as those of the present applicant, or that the properties recited in the present claims would be inherent (such inherency is clearly disproved by the Comparative Examples reported in the present specification).

Moreover, the process conditions employed in Comparative Examples 1 and 2 were identical to those employed in the Example (differing starting materials were employed) and the Comparative Examples *did not* achieve primary particles having substantially octahedral shape, whereas the Example *did* achieve such primary particles. Accordingly, the Comparative Examples reported in the present specification are closer to the present invention than are the various disclosures in Zhong '104, thereby further disproving the notion of inherency advanced in the Office Action.

In addition, the U.S. PTO points to no disclosure in Zhong '104 which would motivate one of skill in the art to make selections from within the generic disclosure in Zhong '104 so as to attempt to produce positive electrode active material having the morphology as recited in the present claims.

In addition, Zhong '104 does not disclose or suggest welding a plurality of current collecting portions directly to the positive electrode or welding a plurality of current collecting portions directly to the negative electrode. The welding of a plurality of current collecting portions directly to the positive electrode (recited in claims 13 and 17) and the welding of a plurality of current collecting portions directly to the negative electrode (recited in claim 13) contribute to the reduction of internal resistance according to the present invention.

The June 28, 2005 Office Action contains a statement that

Zhong et al (US Pat. No. 5,631,104) does not disclose welding a plurality of current collecting portions directly to the positive electrode and to the negative electrode and that the battery has a capacity of 2 Ah, and that the battery is used in an electric vehicle or a hybrid electric vehicle.

(June 28, 2005 Office Action, page 15, lines 15-18).

The U.S. PTO relies on Zhong '597 for alleged disclosure of a lithium battery as a high energy density source for an electric vehicle (June 28, 2005 Office Action, page 15, lines 19-20), and the U.S. PTO relies on Watanabe '975 for alleged disclosure of ultrasonically welding a plurality of tabs directly to the positive electrode and to the negative electrode (June 28, 2005 Office Action, page 16, lines 11-14).

Neither the alleged disclosure in Zhong '597 relied on in the June 28, 2005 Office Action nor the alleged disclosure in Watanabe '975 relied on in the June 28, 2005 Office Action contains any suggestion or motivation to modify the methods or materials employed in Zhong '104 so as to arrive at a method in which primary particles of the positive electrode active material have a substantially octahedral shape constituted mainly by flat crystal faces, the primary particles including particles having at least one side of each flat crystal face of length of 1 μm or

more. In addition, the batteries disclosed in Watanabe '975 differ in many ways from the batteries disclosed in Zhong '104, and Watanabe '975 does not contain disclosure which would indicate that welding current collecting portions directly to the positive electrode of Zhong '104 would achieve any advantage.

Accordingly, no combination of Zhong' 104, Zhong '597 and Watanabe '975 would render obvious any of the subject matter recited in claims 11-14 and 16-21 and 23.

Issue 5 Rejection of claims 11-14 and 16-21 and 23 under 35 U.S.C. §103(a) over U.S. Patent No. 5,961,949 (Manev '949) in view of Zhong '597 and Watanabe '975.

Manev '949 discloses a method for preparing spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_{4+y}$ intercalation compounds (Manev '949, abstract). Manev '949 does not disclose that the particles disclosed therein have any particular shapes.

The June 28, 2005 Office Action includes a statement that

[s]ince Manev et al. disclose identical synthesis conditions and formula for the positive electrode active material in the lithium battery as those of the applicants as discussed above, the properties cited in the instant claims . . . are inherent in the positive electrode active material of Manev et al.

(June 28, 2005 Office Action, page 17, lines 14-17).

Again, as discussed above, and as demonstrated in the Example and Comparative Examples in the present specification, processing positive electrode active material and satisfying merely the features described in the present specification, page 11, lines 5-10 (namely, firing a raw material mixture consisting of oxides of various elements, including Li, Mn and as necessary, a substitution element(s) and an addition element(s), in an oxidizing atmosphere at

700 to 900 °C), does not *inherently* result in production of positive electrode active material having the characteristics recited in the present claims.

As noted above, the specification includes description of an Example in accordance with the present invention, in which a positive electrode active material was produced which consisted of primary particles having a substantially octahedral shape. The procedures described in Manev '949 clearly differ from the method used in the Example. There is clearly no basis for the statements in the Office Action to the effect that Manev '949 discloses identical synthesis conditions and formulas as those of the present applicant, or that the properties recited in the present claims would be inherent (such inherency is clearly disproved by the Comparative Examples reported in the present specification).

Moreover, as noted above, the Comparative Examples reported in the present specification (in which primary particles having substantially octahedral shape *were not* obtained) are closer to the present invention than are the various disclosures in Manev '949, thereby further disproving the notion of inherency advanced in the Office Action.

In addition, the U.S. PTO points to no disclosure in Manev '949 which would motivate one of skill in the art to make selections from within the generic disclosure in Manev '949 so as to attempt to produce positive electrode active material having the morphology as recited in the present claims.

In addition, Manev '949 does not disclose or suggest welding a plurality of current collecting portions directly to the positive electrode or welding a plurality of current collecting portions directly to the negative electrode. The welding of a plurality of current collecting portions directly to the positive electrode (recited in claims 13 and 17) and the welding of a

plurality of current collecting portions directly to the negative electrode (recited in claim 13) contribute to the reduction of internal resistance according to the present invention.

The June 28, 2005 Office Action contains a statement that

Manev et al does not disclose welding a plurality of current collecting portions directly to the positive electrode and to the negative electrode and that the battery has a capacity of 2 Ah, and that the battery is used in an electric vehicle or a hybrid electric vehicle.

(June 28, 2005 Office Action, page 18, lines 3-5).

The U.S. PTO relies on Zhong '597 for alleged disclosure of a lithium battery as a high energy density source for an electric vehicle (June 28, 2005 Office Action, page 18, lines 6-7), and the U.S. PTO relies on Watanabe '975 for alleged disclosure of ultrasonically welding a plurality of tabs directly to the positive electrode and to the negative electrode (June 28, 2005 Office Action, page 18, lines 20-21).

Neither the alleged disclosure in Zhong '597 relied on in the June 28, 2005 Office Action nor the alleged disclosure in Watanabe '975 relied on in the June 28, 2005 Office Action contains any suggestion or motivation to modify the methods or materials employed in Manev '949 so as to arrive at a method in which primary particles of the positive electrode active material have a substantially octahedral shape constituted mainly by flat crystal faces, the primary particles including particles having at least one side of each flat crystal face of length of 1 μm or more. In addition, the batteries disclosed in Watanabe '975 differ in many ways from the batteries disclosed in Manev '949, and Watanabe '975 does not contain disclosure which would indicate that welding current collecting portions directly to the positive electrode of Manev '949 would achieve any advantage.

Accordingly, no combination of Manev '949, Zhong '597 and Watanabe '975 would render obvious any of the subject matter recited in claims 11-14 and 16-21 and 23.

Issue 6 **Rejection of claim 24 under 35 U.S.C. §103(a) over Zhong '104 in view of Zhong '597 and Watanabe '975, further in view of U.S. Patent No. 5,686,203 (Idota '203).**

The June 28, 2005 Office Action includes a statement that:

Zhong et al. ('104) as modified by Zhong et al. ('597) and Watanabe et al. teach all the limitations of claim 24 except that the positive electrode further comprises acetylene black.

(June 28, 2005 Office Action, page 19, lines 11-13).

For the reasons detailed above, the applicants disagree, i.e., none of the applied references, taken individually or in any combination, disclose or suggest positive electrode active material having the morphology as recited in claim 13, from which claim 24 depends.

Idota '203 is relied on in the June 28, 2005 Office Action for alleged disclosure of a positive electrode which can comprise a conductivity imparting agent which may be carbon black or acetylene black, and that acetylene black is preferred.

Any such disclosure in Idota '203 would not overcome the shortcomings of Zhong '104, Zhong '597 and Watanabe '975 as those references are attempted to be applied against claim 13, from which claim 24 depends (namely, Zhong '104, Zhong '597 and Watanabe '975, taken individually or in any combination, fail to disclose or suggest positive electrode active material having the morphology as recited in claim 13).

Accordingly, no combination of Zhong '104, Zhong '597, Watanabe '975 and Idota '203 would render obvious any of the subject matter recited in claim 24.

Issue 7 Rejection of claim 24 under 35 U.S.C. §103(a) over Manev ‘949 in view of Zhong ‘597 and Watanabe ‘975, further in view of U.S. Patent No. 5,686,203 (Idota ‘203).

The June 28, 2005 Office Action includes a statement that:

Manev et al. as modified by Zhong et al. (‘597) and Watanabe et al. teach all the limitations of claim 24 except that the positive electrode further comprises acetylene black.

(June 28, 2005 Office Action, page 20, lines 7-8).

For the reasons detailed above, the applicants disagree, i.e., none of the applied references, taken individually or in any combination, disclose or suggest positive electrode active material having the morphology as recited in claim 13, from which claim 24 depends.

Idota ‘203 is relied on in the June 28, 2005 Office Action for alleged disclosure of a positive electrode which can comprise a conductivity imparting agent which may be carbon black or acetylene black, and that acetylene black is preferred.

Any such disclosure in Idota ‘203 would not overcome the shortcomings of Manev ‘949, Zhong ‘597 and Watanabe ‘975 as those references are attempted to be applied against claim 13, from which claim 24 depends (namely, Manev ‘949, Zhong ‘597 and Watanabe ‘975, taken individually or in any combination, fail to disclose or suggest positive electrode active material having the morphology as recited in claim 13).

Accordingly, no combination of Manev ‘949, Zhong ‘597, Watanabe ‘975 and Idota ‘203 would render obvious any of the subject matter recited in claim 24.

VIII. CLAIMS APPENDIX

Attached hereto as Appendix A is a listing of all of the claims involved in the present appeal.

IX. EVIDENCE APPENDIX

Attached hereto as Appendix B are copies of any evidence submitted pursuant to Sections 1.130, 1.131 or 1.132 of 37 C.F.R., or of any other evidence entered by the examiner and relied upon by appellant in the appeal, along with a statement setting forth where in the record that evidence was entered in the record by the examiner.

X. RELATED PROCEEDINGS APPENDIX

Attached hereto as Appendix C are copies of decisions rendered by a court or the Board in any proceeding identified pursuant to paragraph (c)(1)(ii) of 37 C.F.R. 41.37.

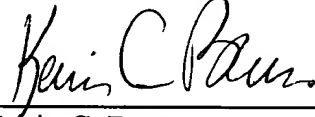
CONCLUSION

Accordingly, the Honorable Board of Patent Appeals and Interferences is respectfully requested to reverse the Final Rejection of claims 11-14, 16-21, 23 and 24 and to pass this application to allowance and issuance.

The Commissioner is hereby authorized to charge any additional fees associated with this communication or credit any overpayment to Deposit Account No. 50-1446.

Respectfully submitted,

BURR & BROWN



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January 13, 2006

Date

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APPENDIX A – CLAIMS ON APPEAL

11. A method of reducing internal resistance of a lithium secondary battery as recited in claim 13, wherein the average primary particle diameter is in the range of from 1 to 20 μm .

12. A method of reducing internal resistance of a lithium secondary battery as recited in claim 13, wherein said primary particles consist essentially of particles having at least one side of each flat crystal face of length of 1 μm or more.

13. A method of reducing internal resistance of a lithium secondary battery, comprising:
forming an electrode body by placing a positive electrode and a negative electrode in contact with a separator, the separator being positioned between the positive electrode and the negative electrode so that the positive electrode is not in contact with the negative electrode, the positive electrode comprising positive electrode active material which comprises Li and Mn and which has a cubic spinel structure, primary particles of the positive electrode active material having a substantially octahedral shape constituted mainly by flat crystal faces, said primary particles including particles having at least one side of each flat crystal face of length of 1 μm or more, the positive electrode active material having a Li/Mn ratio of larger than 0.5;
welding a plurality of current collecting portions directly to said positive electrode; and
welding a plurality of current collecting portions directly to said negative electrode,
said battery having a capacity of 2Ah or more.

14. A method of reducing internal resistance of a lithium secondary battery as recited in claim 13, wherein the primary particles form secondary particles having a maximum particle diameter of 50 μm or less.

16. A method of reducing internal resistance of a lithium secondary battery as recited in claim 13, wherein the battery is used in an electric vehicle or a hybrid electric vehicle.

17. A method of making a lithium secondary battery having low internal resistance, comprising:

welding a plurality of current collecting portions directly to a positive electrode, said positive electrode comprising a positive electrode active material formed by a process comprising:

forming a raw material mixture comprising positive electrode precursor material, said raw material mixture comprising Li and Mn; and

heating said raw material mixture to a temperature and for a time which is effective to convert said raw material mixture into a positive electrode active material having a cubic spinel structure, primary particles of the positive electrode active material having a substantially octahedral shape constituted mainly by flat crystal faces, said primary particles including particles having at least one side of each flat crystal face of length of 1 μm or more;

said battery having a capacity of 2 Ah or more.

18. A method of making a lithium secondary battery having low internal resistance as recited in claim 17, wherein the average primary particle diameter is in the range of from 1 to 20 μm .

19. A method of making a lithium secondary battery having low internal resistance as recited in claim 17, wherein said primary particles consist essentially of particles having at least one side of each flat crystal face of length of 1 μm or more.

20. A method of making a lithium secondary battery having low internal resistance as recited in claim 17, wherein the positive electrode active material has a Li/Mn ratio of larger than 0.5.

21. A method of making a lithium secondary battery having low internal resistance as recited in claim 17, wherein the primary particles form secondary particles having a maximum particle diameter of 50 μm or less.

23. A method of making a lithium secondary battery having low internal resistance as recited in claim 17, wherein the battery is used in an electric vehicle or a hybrid electric vehicle.

24. A method of reducing internal resistance of a lithium secondary battery as recited in claim 13, wherein said positive electrode further comprises acetylene black.

U.S. Application Serial No. 09/997,604



APPENDIX B – EVIDENCE APPENDIX

U.S. Application Serial No. 09/997,604

APPENDIX C – RELATED PROCEEDINGS APPENDIX

NONE

U.S. Application Serial No. 09/997,604

APPENDIX D – ENGLISH-LANGUAGE TRANSLATION OF JAPANESE 08-217452 (JP ‘452) PROVIDED BY THE U.S. PTO

PATENT ABSTRACTS OF JAPAN

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(21)Application number : 07-047924

(71)Applicant : TOSOH CORP

(22)Date of filing : 14.02.1995

(72)Inventor : OKADA MASAKI
YOSHIDA SETSUO

(54) NEEDLE MANGANESE COMPLEX OXIDE, PRODUCTION AND USE THEREOF

(57)Abstract:

PURPOSE: To obtain a new complex oxide by firing a mixture of manganese dioxide of γ -type crystalline structure with a Li compound and at least one of metallic materials selected from Ni, Co, Fe and Cr.

CONSTITUTION: Manganese dioxide of γ -type crystalline structure having a BET specific surface area of 150-500m², a lithium compound and at least one of metallic material selected from Ni, Co, Fe and Cr are mixed. This mixture is subjected to the first heat treatment at a temperature lower than 500°C in the air and/or oxygen for 10 or more hours, then to the second heat treatment at 500-850°C for 10 or more hours to give a manganese complex oxide of the formula: $\text{LiMxMn}_{2-x}\text{O}_4$ (M is Ni, Co, Fe, Cr; $0.0 < x \leq 0.5$) having a spinel type crystalline structure, particles sizes of 10 or less μm , a lattice constant of less than 8.24Å; and a BET specific surface area of 1 or more m²/g. This composite oxide is used as a positive electrode active substance, while Li or Li alloy is used as a negative electrode active substance to easily and inexpensively give a Mn-Li secondary cell using a non-aqueous electrolyte.

LEGAL STATUS

[Date of request for examination]

01.02.2002

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the
examiner's decision of rejection or application
converted registration]

[Date of final disposal for application]

<http://www1.ipdl.jpo.go.jp/PA1/result/detail/main/wAAAa18089DA408217452P1.htm>

2/26/03

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] The manganese multiple oxide to which it becomes from a particle with a particle size of 10 micrometers or less, and the crystal structure is a spinel type and a BET specific surface area is expressed $1\text{m}^2 / \text{above g}$ by chemical formula $\text{LiMX Mn}_2\text{-X O}_4$ (the inside M of a formula is at least one or more kinds chosen from nickel, Co, Fe, and Cr, and is $0.0 < x \leq 0.5$).

[Claim 2] The manganese multiple oxide according to claim 1 whose lattice constant is less than 8.24Å.

[Claim 3] The manufacture method of the manganese multiple oxide of the claim 1 characterized by calcinating the mixture of manganese dioxide and the lithium compound in which a BET specific surface area has gamma type crystal structure of $150\text{m}^2 / \text{g}$ to $500\text{m}^2 / \text{g}$, and at least one or more kinds of metallic materials chosen from nickel, Co, Fe, and Cr.

[Claim 4] The manufacture method of the manganese multiple oxide of a claim 4 that a lithium compound is characterized by being a lithium nitrate.

[Claim 5] The manufacture method of the manganese multiple oxide of a claim 4 that the metallic material of nickel, Co, Fe, and Cr is characterized by being those nitrates.

[Claim 6] The manufacture method of the manganese multiple oxide of the claim 4 characterized by performing 2nd heat treatment at 500-degree-C or more temperature of 850 degrees C or less in baking in the manufacture method of the manganese multiple oxide of a claim 3 after performing 1st heat treatment at the temperature of 500 degrees C or less.

[Claim 7] The lithium secondary battery characterized by using for a negative-electrode active material the compound which can occlusion emit a lithium, a lithium alloy, or a lithium, using nonaqueous electrolyte for an electrolyte, and using the manganese multiple oxide of a claim 1 for a positive active material.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention is a thing about a new manganese multiple oxide, its manufacture method, and its use. in detail It consists of a particle with a particle size of 10 micrometers or less, a BET specific surface area 1m² / above g The crystal structure is a spinel type and it is chemical formula LiMX Mn₂-X O₄ (the inside M of a formula is at least one or more kinds chosen from nickel, Co, Fe, and Cr, and is 0.0 < x ≤ 0.5). The manganese multiple oxide expressed, It is related with the lithium secondary battery which uses the manufacture method and this manganese multiple oxide for a positive active material.

[0002] Since a manganese multiple oxide is cheap, abundant in the manganese of a raw material also in resources and still easier to compound, it is a material which attracts attention most in the positive-active-material material for lithium secondary batteries.

[0003] Since a lithium secondary battery can constitute the cell of high-energy density theoretically, the research and development which aimed at highly efficient-ization also including what was already put in practical use partly as a new style rechargeable battery which bears the next generation are furthered actively.

[0004]

[Description of the Prior Art] With the spread of a personal youth's cordless devices, it is small and lightweight and development of a lithium secondary battery with a high energy density is demanded strongly.

[0005] Recently, development of the lithium ion type rechargeable battery using the compound which can occlusion emit lithium ions, such as a carbonaceous material metallurgy group oxide, is positively furthered for the purpose of safety reservation, without using a lithium metal and a lithium alloy for a negative electrode.

[0006] For this reason, it is necessary for the positive active material to use the compound containing the lithium.

[0007] LiMO₂ in which a basic skeleton has the layer structure which a lithium and transition metals arranged regularly with rock salt structure as a compound which contained the lithium now The type oxide (M is transition metals here) attracts attention. Also in it, research and development are actively furthered including utilization in part from a lithium cobalt oxide (it being written as the following LiCoO₂) and a lithium nickel oxide (it being written as the following LiNiO₂) showing a 4V class cell voltage.

[0008] However, LiCoO₂ That it is related and a cobalt raw material is expensive and LiNiO₂ It is related and the trouble that composition is difficult is already pointed out.

[0009] As a material which shows a 4V class cell voltage in addition to the two above-mentioned material, it is the lithium manganese spinel (it is written as the following LiMn₂O₄) of a spinel type structure. It is known.

[0010] LiMn₂O₄ LiCoO₂ since composition is easy, and moreover abundant in manganese raw materials also in resources and cheap LiNiO₂ It is expected as a material to replace.

[0011] LiMn₂O₄ It is Spinel structure and a lithium is the compound of the normal-spinel type with which manganese occupied 16d site and oxygen occupied 32e site for the spinel 8a site.

[0012] In other words, it has the structure in which the lithium occupied one eighth of the tetrahedral sites of cubic-closest-packing oxygen, and manganese occupied one half of octahedral sites.

[0013] This LiMn₂O₄ When it uses for the positive active material of a lithium secondary battery, it is shown clearly that there are a field which functions on the voltage of about 4 V, and a field which operates on the voltage of about 3 V (135 or small ** et al., collection [of the 29th cell debate lecture summaries], and P1988).

[0014] In the field which functions on the voltage of about 4 V, it is LiMn₂O₄. The lithium ion in a crystal lattice moves through 16c site of an empty oxygen octahedral site in the lithium occupancy site in the crystal structure, and the reaction which goes in and out, without destroying structure where the cubic of the original skeletal structure is

maintained progresses.

[0015] On the other hand, in the field which functions on the voltage of about 3 V, it is LiMn 2O₄. The reaction to which a lithium ion frequents 16c site of the oxygen octahedral site of the empty in a crystal lattice with the change to a tetragonal phase from the cubic of the crystal structure progresses.

[0016] In order to constitute a lithium secondary battery with an energy density high between the two above-mentioned reactions, it is important to use the field which shows the voltage of about 4 V.

[0017] It is LiMn 2O₄ in the field which shows the voltage of about 4 V. When it is made to function, as mentioned above, from a charge-and-discharge reaction progressing without change of crystal system, where the cubic structure of a basic skeleton is maintained, the reversible reaction was expected and the proposal of application to a lithium secondary battery has so far accomplished many.

[0018] However, a rechargeable battery with a high energy density cannot be constituted from an old proposal, and it has not yet resulted by utilization.

[0019] It is LiMn 2O₄ in the field which shows the voltage of about 4 V. Although a charge-and-discharge reaction progresses where cubic structure is maintained when it is made to function, although it is [some], expansion and contraction of a crystal lattice take place by the oxidation reduction of manganese, and receipts and payments of a lithium ion.

[0020] According to examination of this invention persons, it is LiMn 2O₄. Although it is then gradually when the cycle of charge and discharge, i.e., the volume change by expansion and contraction of this crystal lattice, is repeated. The conductive fall accompanying decay of the local crystal structure, detailed-izing of a particle, and detailed-izing and the conductive fall considered to originate in a poor contact with electric conduction assistants (for example, acetylene black, graphite, etc.) further take place, and, for this reason, the fall of the capacity accompanying a charge-and-discharge cycle takes place.

[0021] Furthermore, it is LiMn 2O₄ in the field which shows the voltage of about 4 V when charge and discharge are performed at a high charge-and-discharge rate. Even if it has regulated discharge voltage so that it may be made to function, by repeating charge and discharge Reduction goes to the field which shows the voltage of about 3 V partly, the above-mentioned conductive fall is accelerated because transition of the crystal structure takes place, the utilization factor of a positive active material becomes uneven by the conductive fall of a positive electrode etc., and it is thought that reversibility falls remarkably.

[0022] The above reason to LiMn 2O₄ It is judged that it has not yet resulted by utilization.

[0023] As a method of solving this trouble, the way other elements replace some manganese is proposed.

[0024] For example, in JP,3-219571,A and JP,4-160769,A, LiX MY Mn (2-Y) O₄ ($0.85 \leq x \leq 1.15$, $0.02 \leq y \leq 0.5$) which replaced some manganese by at least one kind of Co, Cr, and Fe is proposed.

[0025] These proposals are replacing some manganese by Co, Cr, and Fe, are making a lattice constant small and making the crystal structure firmer, and aim at preventing destruction of the crystal structure, i.e., the fall of service capacity.

[0026] However, even if saying [making the crystal structure firmer] can make the flexibility over the volume change of the crystal lattice by the charge-and-discharge reaction able to fall and it can reduce degradation speed, the fall of service capacity is still difficult to protect.

[0027] Furthermore, by these proposals, since the particle of the compound which is compounding each at 900 degrees C and is obtained at this temperature was large, when it is used for a positive active material, detailed-ization of the particle by charge and discharge becomes easy to progress, and a capacity fall tends to take place.

[0028] On the other hand, in JP,5-36412,A, it has proposed being LiX Mn (2-X) O₄ which replaced some manganese by at least one kind of Fe and Cr (A being Fe and/or Cr, and $0.1 \leq X \leq 0.4$), in Fe, being 650 degrees C or more 800 degrees C or less, and heat-treating at 650-degree-C or more temperature of 850 degrees C or less in Cr.

[0029] However, by this proposal, it is Mn 2O₃ to a manganese raw material. According to [are using it and] examination of this invention persons, it is Mn 2O₃. When using and compounding at the temperature of 650 degrees C or more, the particle diameter of the compound obtained is large, detailed-ization of the particle by charge and discharge becomes easy to progress, and a capacity fall tends to take place.

[0030] As mentioned above, LiMn 2O₄ proposed until now With the compound which replaced some manganese by other elements, it has not resulted in utilization the place which the cycle property at the time of using for the positive active material of a lithium secondary battery is inadequate, and is former.

[0031] On the other hand, with the spread of a personal youth's cordless devices, it is small and lightweight and development of a lithium secondary battery with a high energy density is demanded strongly.

[0032] By present, it is LiCoO₂ to a positive active material. Although the lithium secondary battery of the ion type

which used carbonaceous material for the negative electrode and used nonaqueous electrolyte for the electrolyte is put in practical use, in order to make it spread broadly as a noncommercial small power supply or an on-site type power supply for power storage, development of a cheaper and more stable lithium secondary battery is desired.

[0033]

[Problem(s) to be Solved by the Invention] The purpose of this invention is new LiMn_2O_4 . It is in offering the manganese system lithium secondary battery which proposed the compound which replaced some manganese by other elements, and its manufacture method, and used this compound for the positive active material further and which was excellent in the cycle property.

[0034]

[Means for Solving the Problem] As a result of this invention persons' inquiring wholeheartedly for the purpose of solving the above-mentioned technical problem, it consists of a new manganese multiple oxide, i.e., a particle with a particle size of 10 micrometers or less, and BET specific surface areas are more than $1\text{ m}^2/\text{g}$. The crystal structure is a spinel type and it is chemical formula $\text{LiMX Mn}_2\text{-XO}_4$ (the inside M of a formula is at least one or more kinds chosen from nickel, Co, Fe, and Cr). The manganese multiple oxide expressed with $0.0 < x \leq 0.5$ is found out for the first time. the manganese multiple oxide The BET specific surface area found out the thing which calcinate the mixture of manganese dioxide and the lithium compound which have gamma type crystal structure of $150\text{ m}^2/\text{g}$ to $500\text{ m}^2/\text{g}$, and at least one or more kinds of metallic materials chosen from nickel, Co, Fe, and Cr and for which thing composition can be carried out. Furthermore, it finds out that the manganese system lithium secondary battery which is not in the former and which was excellent in the cycle property can be constituted from using this for the positive active material of a lithium secondary battery, and came to complete this invention.

[0035]

[Function] Hereafter, this invention is explained concretely.

[0036] Chemical formula $\text{LiMX Mn}_2\text{-XO}_4$ (the inside M of a formula is at least one or more kinds chosen from nickel, Co, Fe, and Cr, and is $0.0 < x \leq 0.5$) of this invention The manganese multiple oxide expressed is a manganese multiple oxide of Spinel structure to which at least one or more kinds of metals with which a lithium is chosen from manganese, and nickel, Co, Fe and Cr in one half of octahedral sites occupied one eighth of the tetrahedral sites of cubic-closest-packing oxygen.

[0037] The manganese multiple oxide of this invention is LiMn_2O_4 which the position of a diffraction peak shifted to the angle-of-elevation side. An analogous X diffraction pattern is shown. That is, a crystal lattice is LiMn_2O_4 . It is the manganese multiple oxide which became small.

[0038] According to examination of this invention persons, it is LiMn_2O_4 by the valence and ion size of a substitution metal. It becomes a manganese multiple oxide with a small crystal lattice.

[0039] When nickel replaces some manganese, since the stable phase as an oxide of nickel is NiO , nickel is replaced by some manganese as + divalent, it is that the + trivalent manganese in a compound oxidizes to + tetravalence, and contraction of a crystal lattice produces it.

[0040] When it replaces by Co, since the stable phase as an oxide of Co is CoO or Co_3O_4 , a part of Co replaces by some manganese as + trivalent as + divalent. + when the effect that + trivalent manganese oxidizes to + tetravalence when replacing as divalent replaces as + trivalent, the contraction which is a crystal lattice arises also in one of cases, and the case of both hybrid models according to the effect replaced by Co with an ionic radius smaller than manganese

[0041] the case where it replaces by Fe and Cr -- the stable phase as an oxide -- respectively -- Fe_2O_3 And Cr_2O_3 it is -- it replaces by some manganese as + trivalent from things, respectively Contraction of a crystal lattice arises according to the effect replaced by Fe and Cr with an ionic radius smaller than manganese.

[0042] By the above effect, a crystal lattice is LiMn_2O_4 . It is thought that it becomes small. Furthermore, the rate of contraction of the crystal lattice by the amount of substitution changes from the above thing with the kinds and the amounts of substitution of a metallic material to replace, respectively.

[0043] In addition, even if it is trespassing upon a lithium site, and + divalent when an ionic radius is too small, although there is a metal which forms a stable oxide with a metal with an ionic radius smaller than manganese, and + divalent besides nickel, Co, Fe, and Cr, when an ionic radius is too large, since a substitution reaction cannot occur easily, nickel, Co, Fe, and Cr which are proposed this time are considered to be the most excellent substitution metal.

[0044] For the manganese multiple oxide of this invention, a crystal lattice is LiMn_2O_4 . Although it is a small compound, a crystal lattice is with a bird clapper small, and is considered that there are the following effects. When making the amount of the + trivalent manganese in a compound decrease fundamentally and making it function on the voltage of about 4 V, the amount of replace [some manganese / by at least one kind of nickel, Co, Fe, and Cr] of the manganese which participates in an oxidation-reduction reaction decreases. In other words, a charge-and-discharge

reacting weight will be restricted, therefore the amount of expansion / contraction of a crystal lattice becomes small, and it is thought that a cycle property improves.

[0045] According to examination of this invention persons, some manganese by furthermore, the thing to replace by at least one kind of nickel, Co, Fe, and Cr If discharge voltage is regulated so that it may be made to function in the field which a charge-and-discharge reaction progresses uniformly by the whole active material, and shows the voltage of about 4 V even when the crystal structure becomes the compound which progressed uniformly and charge and discharge are performed at a high charge-and-discharge rate for this reason It comes to function in reversible, without a reduction reaction going to the field which shows the voltage of about 3 V.

[0046] As for the size of a crystal lattice, it is more desirable that it is 8.10Å or more in less than 8.24Å that it is less than 8.24Å desirable in more detail.

[0047] When the size of a crystal lattice uses for the positive active material of a lithium secondary battery in 8.24Å or more, expansion and contraction of the crystal lattice accompanying charge and discharge become large, and decay of the crystal structure promotes.

[0048] On the other hand, if a crystal lattice is less than 8.24Å, expansion and contraction of the crystal lattice accompanying charge and discharge will become small, and its cycle property will improve.

[0049] If a crystal lattice becomes not much small too much, since the diffusion within solid phase of a lithium will be in a difficult state, in connection with charge and discharge, destruction of a crystal lattice becomes easy to take place.

[0050] According to examination of this invention persons, when a high power type lithium secondary battery is constituted, it turns out that 8.10Å or more is desirable.

[0051] The amount of substitution at the time of replacing by at least one kind of nickel, Co, Fe, and Cr is chemical formula $\text{LiMX Mn}_{2-x}\text{O}_4$. It is indispensable that the value of X at the time of expressing is 0.5 or less or more in 0.0, and 0.2 or less are more desirable in more detail at 0.05 or more.

[0052] While the crystal lattice of the compound obtained becomes small too much as stated previously when the value of X exceeds 0.5, composition of the compound of spinel single phase becomes difficult.

[0053] Moreover, when it constitutes the lithium secondary battery of high capacity, since required, the thing for which both charge-and-discharge capacity and a cycle property are reconciled and which make the value of X 0.2 or less or more by 0.05 is more desirable.

[0054] The manganese multiple oxide expressed with chemical formula $\text{LiMX Mn}_{2-x}\text{O}_4$ (the inside M of a formula is at least one or more kinds chosen from nickel, Co, Fe, and Cr, and is $0.0 < x \leq 0.5$) of this invention makes it indispensable to consist of particles with a particle size of 10 micrometers or less.

[0055] Although it is unknown about a detail, since it is a particle with a particle size of 10 micrometers or less, when it uses for the positive active material of a lithium secondary battery, it becomes easy to absorb expansion and contraction of the crystal lattice accompanying charge and discharge between particles, and the conductive fall considered to originate in a poor contact with an electric conduction assistant can be suppressed.

[0056] Although it will not be restricted especially if it is 10 micrometers or less, when the restoration nature as a positive active material is taken into consideration, a particle diameter can maintain the restoration nature as a positive-electrode material with restricting to 10 micrometers from 1 micrometer, and a bird clapper to this range is desirable in composition of a high capacity type rechargeable battery being possible.

[0057] As for the size of the surface area of the manganese multiple oxide expressed with chemical formula $\text{LiMX Mn}_{2-x}\text{O}_4$ (the inside M of a formula is at least one or more kinds chosen from nickel, Co, Fe, and Cr, and is $0.0 < x \leq 0.5$) of this invention, a BET specific surface area makes it indispensable for a BET specific surface area to be more than 1 m²/g.

[0058] Even when the value of a BET specific surface area used the compound 1 m² / more than g for the positive active material of a lithium secondary battery, and contact to an electric conduction assistant and the electrolytic solution becomes good and performs charge and discharge at a high charge-and-discharge rate, a charge-and-discharge reaction progresses uniformly by the whole active material, and the rechargeable battery which excelled [type / high capacity] in the cycle property can be constituted.

[0059] When the restoration nature as a positive active material is taken into consideration, the restoration nature as a positive-electrode material can maintain with restricting the value of a BET specific surface area to below 10 m² / g, the composition of a high capacity type rechargeable battery is attained, and especially between 5 m² / g to 10 m² / g is desirable.

[0060] In the manufacture method of the manganese multiple oxide of this invention, it is indispensable to use manganese dioxide in which a BET specific surface area has gamma type crystal structure of 150 m² / g to 500 m² / g as a source of manganese.

[0061]. while a reaction progresses uniformly and particle growth is notably suppressed by using manganese dioxide in which a BET specific surface area has gamma type crystal structure of 150m² / g to 500m² / g as a source of manganese -- composition -- a uniform manganese multiple oxide becomes compoundable

[0062] Although the detail of mechanism ***** of this reaction is not clear, it thinks as follows. Since the surface area is very large, manganese dioxide in which the BET specific surface area used by this invention has gamma type crystal structure of 150m² / g to 500m² / g has very high reactivity with a lithium compound. Therefore, it is easy to generate the manganese multiple oxide of uniform composition.

[0063] Moreover, since manganese dioxide in which the crystal structure has the gamma type crystal structure has the channel structure of (1x2) and the diffusion path inside [of a lithium] a crystal is secured, when it is made to react with a lithium compound, it is thought that a reaction advances easily. Furthermore, although the reason is unknown, since the surface area is very large, it is thought that composite-ization with a metallic material also advances easily and the manganese multiple oxide of uniform composition tends to generate it.

[0064] This effect has a remarkable BET specific surface area from 150m² / g to 500m² / g. This is considered to be ***** by the following reason.

[0065] It becomes difficult for a BET specific surface area to be unable to perform sufficiently uniformly mixture with manganese dioxide, a lithium compound, and a metallic material, but to manufacture the manganese multiple oxide of uniform composition by under 150m² / g.

[0066] the case where a BET specific surface area exceeds 500m² / g -- the way of the heat phase transition of manganese dioxide -- a composite-ized reaction with a lithium compound and a metallic material -- happening -- being easy -- since the channel structure which that it is easy (1x2) diffuses [a lithium] can distort -- a composite-ized reaction -- progressing -- being hard -- while it becomes difficult to manufacture the manganese multiple oxide of uniform composition -- condensation of a particle -- happening -- being easy -- a manganese multiple oxide 10 micrometers or less cannot be

[0067] Since it stated above, if a BET specific surface area uses for the source of manganese manganese dioxide which has gamma type crystal structure of 150m² / g to 500m² / g, it will be thought that a manganese multiple oxide with uniform composition can be manufactured easily.

[0068] Manganese dioxide in which the BET specific surface area used by this invention has gamma type crystal structure of 150m² / g to 500m² / g can be manufactured by the thing which is shown in JP,41-1696,B and which perform an electrolysis reaction with the usual sulfuric-acid concentration higher than the manufacture conditions and the usual high current density of an electrolytic manganese dioxide so that it may be.

[0069] On the usual manufacture conditions, an electrolytic manganese dioxide deposits in the shape of an anode plate by the oxidation reaction shown in (1) formula.

[0070]

$$\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \quad (1)$$

For this reason, after an electrolysis end, although trituration processing is performed and it considers as a style or manganese at the shape's of a particle after exfoliating from an anode plate, the BET specific surface areas of manganese dioxide obtained by this method are below 100m² / g.

[0071] On the other hand, manganese dioxide of gamma type crystal structure used by this invention makes only Mn³⁺ ion an anode plate product, as it is making high sulfuric-acid concentration in the electrolytic solution, the stability of Mn³⁺ ion is made to increase and it is shown in (2) formulas rather than the manufacture conditions of the usual electrolytic manganese dioxide, and it is (3) in the electrolytic solution. It is manufactured by making the adding-water decomposition reaction shown by the formula perform.

[0072]

$$\text{Mn}^{2+} \rightarrow \text{Mn}^{3+} + \text{e}^- \quad (2)$$

$$2\text{Mn}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + \text{Mn}^{2+} + 4\text{H}^+ \quad (3)$$

By the above-mentioned method, manganese dioxide in which a BET specific surface area has gamma type crystal structure of 150m² / g to 500m² / g can be manufactured.

[0073] What thing may be used for them as long as the lithium material used for manufacture of the manganese multiple oxide of this invention is a lithium and/or a lithium compound. For example, although a lithium metal, a lithium hydroxide, a lithium oxide, a lithium carbonate, an iodation lithium, a lithium nitrate, an oxalic acid lithium, an alkyl lithium, etc. are illustrated, especially a lithium nitrate is more desirable preferably also what is fused at the temperature of 500 degrees C or less, and in it.

[0074] What thing may be used for them as long as the metallic materials used for manufacture of the manganese multiple oxide of this invention are a metal and/or metallic compounds. For example, although the hydroxide of a metal

and a metal, a metal oxide, a metal carbonate, a metal nitrate, an organometallic complex, etc. are illustrated, especially a metal nitrate is more desirable preferably also what is fused at the temperature of 500 degrees C or less, and in it.

[0075] Especially the mixed method of manganese dioxide and the lithium compound in which a BET specific surface area has gamma type crystal structure of 150m² / g to 500m² / g, and at least one or more kinds of metallic materials chosen from nickel, Co, Fe, and Cr is not restricted, and should just be mixed by solid phase and/or the liquid phase. For example, the method of mixing the powder of the above-mentioned raw material with dry type and/or wet and the method of mixing because a BET specific surface area adds and agitates manganese dioxide which has gamma type crystal structure of 150m² / g to 500m² / g in the solution which dissolved and/or suspended the lithium compound and the metallic material are illustrated. Manganese dioxide and the lithium compound in which a BET specific surface area has gamma type crystal structure of 150m² / g to 500m² / g, The baking method of the manganese multiple oxide which calcinates the mixture of at least one or more kinds of metallic materials chosen from nickel, Co, Fe, and Cr Although not restricted especially, after calcinating the 1st heat treatment at the temperature of 500 degrees C or less in the atmosphere and/or oxygen, it is desirable to perform 2nd heat treatment at the temperature of 850 degrees C or less more than the temperature exceeding 500 degrees C.

[0076] According to examination of this invention persons, by the low temperature side, a composite-ized reaction progresses bordering on 500 degrees C, and development of Spinel structure takes place by the elevated-temperature side. Therefore, after fully advancing a composite-ized reaction with the 1st heat treatment first, by performing a crystal-growth reaction with the 2nd heat treatment, composition is more uniform and the manganese multiple oxide from which Spinel structure developed can be compounded. Furthermore, a composite-ized reaction is promoted more by performing 1st heat treatment in the atmosphere and/or oxygen.

[0077] In addition, it is desirable to carry out below 850 degrees C from a bird clapper at the temperature at which the 2nd heat treatment exceeds 850 degrees C that particle growth and the reduction reaction of manganese tend to occur.

[0078] In addition, although not restricted especially concerning a firing time, the 1st heat treatment and the 2nd heat treatment of 10 hours or more are desirable.

[0079] As a negative electrode of the lithium secondary battery of this invention, the compound which can occlusion emit a lithium metal, a lithium alloy, or a lithium can be used. As a lithium alloy, a lithium / tin alloy, a lithium/aluminium alloy, a lithium/lead alloy, etc. are illustrated, for example. moreover -- as the compound which can occlusion emit a lithium -- carbonaceous material, such as graphite and a graphite, FeO and Fe 2O₃, and Fe 3O₄ etc. -- an iron oxide, CoO and Co 2O₃, and Co 3O₄ etc. -- oxides, such as cobalt oxide, are illustrated

[0080] Moreover, the electrolyte of the lithium secondary battery of this invention Although not restricted especially, for example Carbonate, such as a propylene carbonate and diethyl carbonate Lactone, such as sulfolanes, such as a sulfolane and dimethyl sulfoxide, and gamma-butyrolactone In at least one or more kinds of ether, such as dimethoxyethane, of organic solvents What dissolved at least one or more kinds of lithium salt, such as a lithium perchlorate, 4 fluoride lithium borate, a 6 fluoride [phosphoric-acid] lithium, and a trifluoromethane sulfonic-acid lithium, the solid electrolyte of lithium ion conductivity of an inorganic system and an organic system, etc. can be used. It used for the manganese multiple-oxide positive active material obtained by this invention, and the cell shown in drawing 1 was constituted.

[0081] The lead wire for 1:positive electrodes, the mesh for 2:positive-electrode current collection, 3:positive electrode, 4:separator, 5:negative electrode, the mesh for 6:negative-electrode current collection, the lead wire for 7:negative electrodes, and 8:container are shown all over drawing.

[0082] this invention is not limited by these examples although an example is shown as an example of this invention below.

[0083]

[Example] In addition, X diffraction measurement in the example and the example of comparison of this invention, observation of a particulate structure, and measurement of specific surface area were performed by the following methods.

[0084]

X diffraction measurement : Measurement model The Mac Saiensu-Sha Co., Ltd. make MXP3 An irradiation X-ray Cu K alpha rays Measurement mode Step scan Scanning conditions As 2theta, 0.04 degrees Measurement time 5 seconds Measuring range It is 10 degrees to 70 degrees as 2theta. Observation of a particulate structure : [Measurement model] A scanning electron microscope JEOL JSM-T220A Acceleration voltage 15kV Surface-area measurement : Measurement model BET adsorption method specific-surface-area measuring device measuring method Inside of a nitrogen gas air current (the rate of flow : per minute 15 millimeter RITTO RU) Automatic, after processing at 250

degrees C for 40 minutes Surface-area measuring device (ASAmade from Shibata science machine industrial , Inc.-2000) It measured.

[0085] Moreover, the length of a crystallographic axis is the X diffraction measurement data of each compound to the WPPD method (Whole-Powder-Pattern Decomposition Method). It determined.

[0086] Furthermore, the component analysis was measured by the ICP AEM method.

[0087] [Manufacture of a manganese multiple oxide]

As example 1 (manufacture of $\text{LiCo}_0.1\text{Mn}_{1.9}\text{O}_4$) example 1, it is $\text{LiCo}_0.1\text{Mn}_{1.9}\text{O}_4$. It manufactured by the following methods. Pt board is used for an anode plate in the solution which contains a manganese sulfate in 25g [l.]/, and contains a sulfuric acid by the concentration of 150g/l., and it is 50 A/dm². The particle-like electrolytic manganese dioxide was obtained by electrolyzing with current density. This electrolytic manganese dioxide was manganese dioxide with 190m² of BET specific surface areas / g, 1 micrometer or less of particle diameters, and the gamma type crystal structure as a result of analysis.

[0088] Next, this manganese dioxide, lithium-nitrate (special grade chemical), and cobalt-nitrate 6 hydrate (special grade chemical) After mixing so that Li:Mn:Co may be set to 1:1.9:0.1 by the mole ratio, it calcinated at the temperature of 450 degrees C in the atmosphere for 24 hours.

[0089] Next, after lowering this to a room temperature and grinding and mixing with a mortar, it calcinated at the temperature of 650 degrees C in the atmosphere for 24 hours.

[0090] The observation result of a particulate structure was shown in drawing 3, and a chemical-analysis result, the length of a crystallographic axis, and the measurement result of a BET specific surface area were shown for the X diffraction pattern of the obtained compound in Table 1 at drawing 2.

[0091]

[Table 1]

	化学組成	a 軸の長さ (10 ⁻¹⁰ m)	B E T 比表面積 (m ² / g)	容量維持率 (%)
実施例 1	$\text{LiCo}_{0.1}\text{Mn}_{1.9}\text{O}_4$	8.227	8.5	95
実施例 2	$\text{LiCo}_{0.2}\text{Mn}_{1.8}\text{O}_4$	8.219	9.0	98
実施例 3	$\text{LiNi}_{0.1}\text{Mn}_{1.9}\text{O}_4$	8.235	8.3	96
実施例 4	$\text{LiFe}_{0.1}\text{Mn}_{1.9}\text{O}_4$	8.238	7.8	95
実施例 5	$\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4$	8.237	8.2	96
比較例 1	$\text{LiCo}_{0.2}\text{Mn}_{1.8}\text{O}_4$	8.222	0.6	90

[0092] As a result of analysis, for the obtained compound, it consists of grains 5 micrometers or less, and the length of a crystallographic axis is $\text{LiCo}_0.1\text{Mn}_{1.9}\text{O}_4$ of 8.227Å, and 8.5m² of BET specific surface areas / g. It turns out that it is the manganese multiple oxide of the Spinel structure expressed.

[0093] It manufactured like the example 1 except having mixed as example 2 (manufacture of $\text{LiCo}_0.2\text{Mn}_{1.8}\text{O}_4$) example 2, so that Li:Mn:Co might be set to 1:1.8:0.2 by the mole ratio.

[0094] The obtained compound was a manganese multiple oxide of Spinel structure which consists of a particle 5 micrometers or less as a result of analysis.

[0095] A chemical-analysis result, the length of a crystallographic axis, and the measurement result of a BET specific surface area were shown in Table 1.

[0096] As example 3 (manufacture of $\text{LiNi}_0.1\text{Mn}_{1.9}\text{O}_4$) example 3, it is $\text{LiNi}_0.1\text{Mn}_{1.9}\text{O}_4$. It manufactured by the following methods. After mixing nickel nitrate 6 hydrate (special grade chemical) with manganese dioxide manufactured in the example 1, and a lithium nitrate (special grade chemical) so that Li:Mn:nickel may be set to 1:1.9:0.1 by the mole ratio, it calcinated at the temperature of 450 degrees C in the atmosphere for 24 hours.

[0097] Next, after lowering this to a room temperature and grinding and mixing with a mortar, it calcinated at the

temperature of 650 degrees C in the atmosphere for 24 hours.

[0098] As a result of analysis, the obtained compound consists of a 5-micrometer particle, and the length of a crystallographic axis is $\text{LiNi}_{0.1}\text{Mn}_{1.9}\text{O}_{4.0}$ of 8.235A, and 8.3m^2 of BET specific surface areas / g. It turns out that it is the manganese multiple oxide of the Spinel structure expressed. A chemical-analysis result, the length of a crystallographic axis, and the measurement result of a BET specific surface area were shown in Table 1.

[0099] As example 4 (manufacture of $\text{LiFe}_{0.1}\text{Mn}_{1.9}\text{O}_4$) example 4, it is $\text{LiFe}_{0.1}\text{Mn}_{1.9}\text{O}_4$. It manufactured by the following methods. After mixing nine hydrates (special grade chemical) of iron nitrate with manganese dioxide manufactured in the example 1, and a lithium nitrate (special grade chemical) so that $\text{Li}:\text{Mn}:\text{Fe}$ may be set to 1:1.9:0.1 by the mole ratio, it calcinated at the temperature of 450 degrees C in the atmosphere for 24 hours.

[0100] Next, after lowering this to a room temperature and grinding and mixing with a mortar, it calcinated at the temperature of 850 degrees C in the atmosphere for 24 hours.

[0101] As a result of analysis, the obtained compound consists of a particle 10 micrometers or less, and the length of a crystallographic axis is $\text{LiFe}_{0.1}\text{Mn}_{1.9}\text{O}_{4.0}$ of 8.238A, and 7.8m^2 of BET specific surface areas / g. It turns out that it is the manganese multiple oxide of Spinel structure expressed.

[0102] A chemical-analysis result, the length of a crystallographic axis, and the measurement result of a BET specific surface area were shown in Table 1.

[0103] As example 5 (manufacture of $\text{LiCr}_{0.2}\text{Mn}_{1.9}\text{O}_4$) example 5, it is $\text{LiCr}_{0.2}\text{Mn}_{1.8}\text{O}_4$. It manufactured by the following methods. After mixing nine hydrates (special grade chemical) of a chromium nitrate with manganese dioxide manufactured in the example 1, and a lithium nitrate (special grade chemical) so that $\text{Li}:\text{Mn}:\text{Cr}$ may be set to 1:1.8:0.2 by the mole ratio, it calcinated at the temperature of 450 degrees C in the atmosphere for 24 hours.

[0104] Next, after lowering this to a room temperature and grinding and mixing with a mortar, it calcinated at the temperature of 850 degrees C in the atmosphere for 24 hours.

[0105] As a result of analysis, the obtained compound consists of a particle 10 micrometers or less, and the length of a crystallographic axis is $\text{LiCr}_{0.2}\text{Mn}_{1.8}\text{O}_{4.0}$ of 8.237A, and 8.2m^2 of BET specific surface areas / g. It turns out that it is the manganese multiple oxide of the Spinel structure expressed.

[0106] A chemical-analysis result, the length of a crystallographic axis, and the measurement result of a BET specific surface area were shown in Table 1.

[0107] As an example 1 of example of comparison 1 (manufacture of $\text{LiCo}_{0.2}\text{Mn}_{1.8}\text{O}_4$) comparison, it is $\text{LiCo}_{0.2}\text{Mn}_{1.8}\text{O}_4$. It manufactured by the following methods. After mixing Mn_3O_4 (trimanganese tetroxide : special grade chemical) and basic cobalt carbonate (special grade chemical) with a lithium carbonate (special grade chemical) so that $\text{Li}:\text{Mn}:\text{Co}$ may be set to 1:1.8:0.2 by the mole ratio, it calcinated at the temperature of 900 degrees C in the atmosphere for 10 hours. The observation result of a particulate structure was shown in drawing 4, and a chemical-analysis result, the length of a crystallographic axis, and the measurement result of a BET specific surface area were shown for the X diffraction pattern of the obtained compound in Table 1 at drawing 2. As a result of analysis, for the obtained compound, a length of one side consists of a regular-octahedron needlelike particle 1 micrometers or more, and the length of a crystallographic axis is $\text{LiCo}_{0.2}\text{Mn}_{1.8}\text{O}_{3.8}$ of 8.222A **. Although it turns out that it is the manganese multiple oxide of the Spinel structure expressed, BET specific surface areas were $0.6\text{m}^2/\text{g}$.

[0108] It is the mixture (tradename : TAB- 2) of the polytetrafluoroethylene of an electric conduction agent, and acetylene black about the manganese multiple oxide manufactured in [composition of cell] examples 1-5, and the example 1 of comparison. It mixed at a rate of 2:1 by the weight ratio. It is 75mg of mixture 1 ton/cm² At a pressure, it is the mesh (SUS 316) of 20mmphi. After casting in the shape of a pellet upwards, reduced-pressure-drying processing was performed at 200 degrees C for 5 hours.

[0109] This is used for the positive electrode of 3 of drawing 1, the piece of a lithium clipped out from the lithium foil (0.2mm in thickness) is used for the negative electrode of 5 of drawing 1, and it is a lithium perchlorate to propylene carbonate in the electrolytic solution 1 mol/dm³ What was dissolved by concentration is infiltrated into the separator of 4 of drawing 1, and it is 2 the cross section of 2.5cm. The cell shown in drawing 1 was constituted.

[0110] The cell created by the [evaluation of cell performance] above-mentioned method is used, and it is 1.0 mA/cm². With fixed current, the cell voltage repeated charge and discharge between 4.5V and 3.5V.

[0111] It was shown in Table 1, the rate, i.e., the capacity maintenance factor, of the service capacity of 50 cycle eye to the service capacity of 1 cycle eye.

[0112] Although each manganese multiple oxide manufactured in the examples 1-5 showed 95% or more of high maintenance factor, the manganese multiple oxide manufactured in the example 1 of comparison was 90%. A result is shown in Table 1.

[0113]

[Effect of the Invention] As stated above the manganese multiple oxide of the invention in this application It consists of a particle with a particle size of 10 micrometers or less. a BET specific surface area 1m² / above g Chemical formula LiMX Mn₂-X O₄ (the inside M of a formula is at least one or more kinds chosen from nickel, Co, Fe, and Cr) of a spinel type [crystal structure] 0.0 < x ≤ 0.5 It is the new manganese multiple oxide expressed, and if the new manganese multiple oxide is used for a positive electrode, the manganese system lithium secondary battery which is not in the former and which was excellent in the cycle property can be constituted.

[0114] It is useful knowledge on industry to have found out a manganese system positive-electrode material applicable to a lithium secondary battery positive active material.

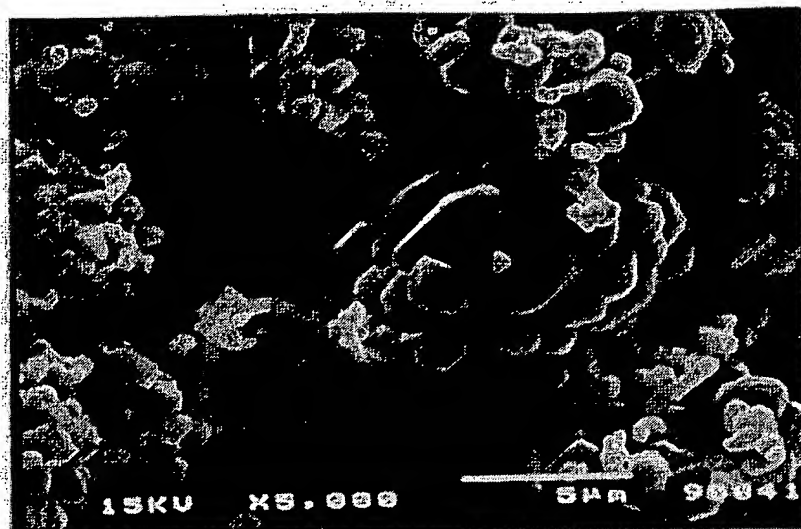
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APPENDIX E – IMAGE OF FIGS. 3 AND 4 OF JAPANESE 08-217452 (JP ‘452)

【図3】

図面代用写真

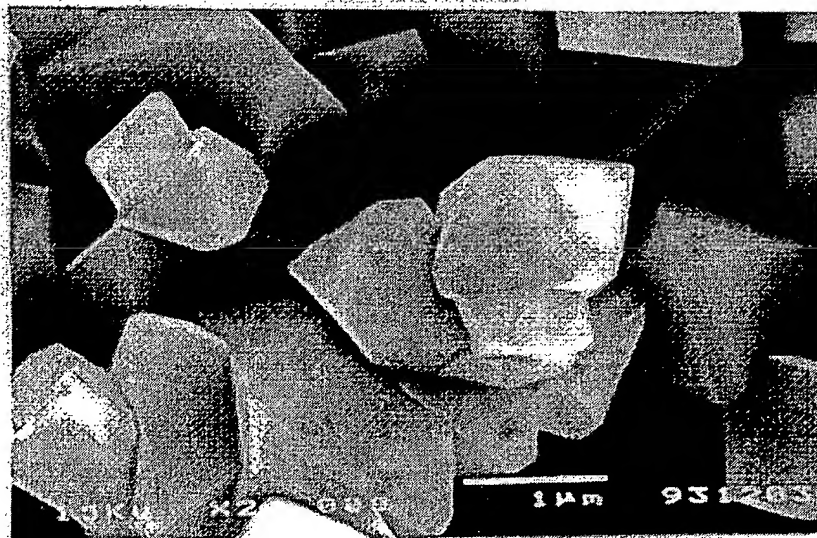


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【図4】

図面代用写真



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U.S. Application Serial No. 09/997,604

APPENDIX F – MARKED-UP IMAGE OF FIGS. 3 AND 4 OF JAPANESE 08-217452 (JP ‘452)

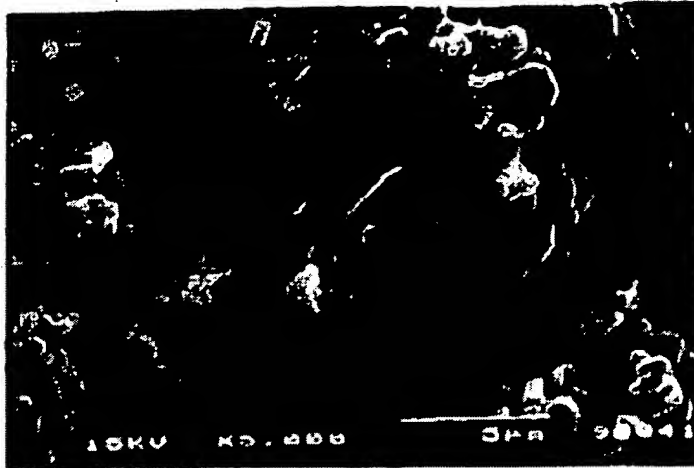
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【図3】



【図4】



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